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Accelerating Oxygen Reduction Catalysts through Preventing Poisoning with Non-Reactive Species by Using Hydrophobic Ionic Liquids

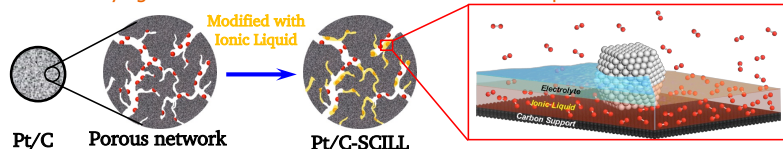


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High cost and poor stability of oxygen reduction reaction (ORR) electrocatalysts are the major barriers for broad-based application of polymer electrolyte membrane fuel cells (PEMFCs). We look beyond directly engineering the structures of active sites and disclose a facile and easy to scale up approach to improving Pt catalyst for ORR, by introducing tiny amounts of hydrophobic ionic liquid (IL) into commercial Pt/C catalyst. The ORR performance of these IL-modified catalysts can be readily manipulated by varying the degree of IL filling (α). Fine-Tuning α resulted in optimized catalyst at $\alpha = 50\%$, whose activity is 3.2 times higher than Pt/C and surpasses the activity target set for 2017-2020. Most recently, we disclose that introduction of a common and inexpensive IL ([Bmim][NTf₂]) to the Pt/C can also accelerate the ORR kinetics by preventing Pt sites from being oxidized and give birth to a Pt/C with record high mass activity (1.01 A mg⁻¹_{Pt}@0.9 V) for pure Pt catalysts. Besides, the IL-modified catalysts exhibit substantially enhanced stability relative to Pt/C. We believe that these findings open a new avenue for catalyst optimization for next-generation fuel cells.

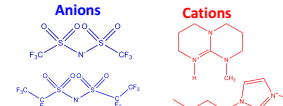
Experimental Section

Synthesis: Modifying the active site microenvironment with ionic liquids

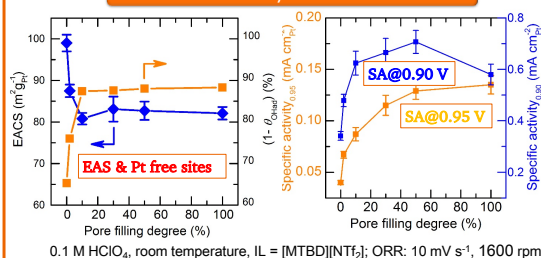


Materials

Catalyst: 20 wt.% Pt/C (JM HISPEC)
Electrolyte: 0.1 M HClO₄
ILs:

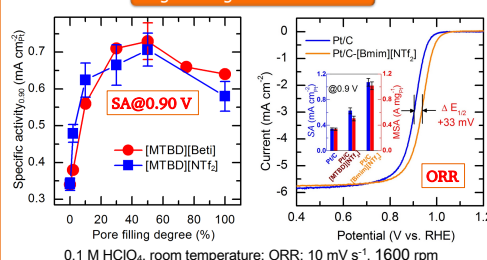


Electrochemical Analysis & ORR Performance



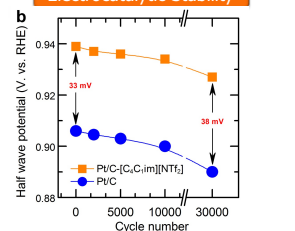
- Introducing IL into Pt/C leads to a reduction in EACS by up to 19%; Number of blocked Pt sites decreases significantly
- At high potential regions, SA increases strongly with pore filling degrees (α), and settles at $\alpha > 50$

Engineering the IL Structure



- Pt activity towards ORR is not sensitive to the O₂ solubility in ILs
- Pt/C-[Bmim][NTf₂] exhibits the record high activity towards ORR, which is three times more active than the pristine Pt/C

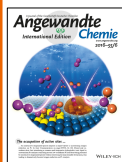
Electrocatalytic Stability



- Very good electrocatalytic stability was observed on the IL modified Pt/C catalyst.

Origin of the Boosting Effect

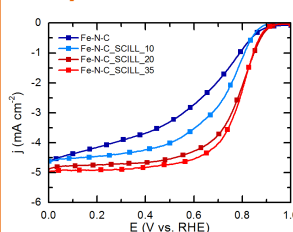
What we can learn...



- The IL phase would selectively locate at the defect /low coordinated Pt sites. (Evidenced by CO-stripping measurements)
- The hydrophobicity of IL would help suppress the surface oxidation of Pt. (Evidenced by CV, Tafel analysis, and CO-stripping)
- The defect sites with IL are still accessible for O₂ molecules.
- Exceeding a certain pore filling degree can lead to a decrease in activity and capacitance, which was also observed for Pt-free Fe-N-C catalysts

Outlook

Transfer of IL modification to non-noble catalysts^[5]



- Non noble Fe-N-C catalysts
- alkaline conditions
- up to 35% pore filling a activity increase correlating with an capacitance increase
- first AST show also a stability increase.

Conclusions

- IL modification is a new methodology to engineer electrocatalysts.**
- Pore diffusion limitation induced by the viscous IL can be reduced through partial filling of the particles.**
- When structure-activity relationships are known, molecular variation of anion and cation can be employed for catalyst tuning.**

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